SYNTHETIC GLYCERIN.[23] The growing market for glycerin, and the fact that it was a coproduct of soap and dependent upon the latter's production, were the incentives for research into methods for producing this trihydroxy alcohol. The process of making glycerin from propylene procured for the Shell Development Co. the 1948 Chemical Engineering achievement award.[24] The propylene is chlorinated at 510°C at 101 kPa to produce allyl chloride in seconds in amounts greater than 85 percent of theory (based on the propylene). Vinyl chloride, some disubstituted olefins, and some 1, 2 and 1, 3-dichloropropanes are also formed. (The reaction producing allyl chloride was new to organic synthesis, involving the chlorination of an olefin by substitution instead of addition.) Treatment of the allyl chloride with hypochlorous acid at 38°C produces glycerin dichlorohydrin ($CH_2Cl \cdot CHCl \cdot CH_2OH$), which can be hydrolyzed by caustic soda in a 6% Na_2CO_3 solution at 96°C. The glycerin dichlorohydrin can be hydrolyzed directly to glycerin, but this takes two molecules of caustic soda; hence a more economical procedure is to react with the cheaper calcium hydroxide, taking off the epichlorohydrin as an overhead in a stripping column. The epichlorohydrin is

[23]ECT, 3d ed., vol. 11, 1980, p. 923; *McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 16, McGraw-Hill, New York, 1982, p. 310.

[24]Hightower, Glycerin from Petroleum, *Chem. Eng.* **55** (9) 96 (1948); Synthetic Glycerin, *Chem. Eng.* **55** (10) 100 (1948).

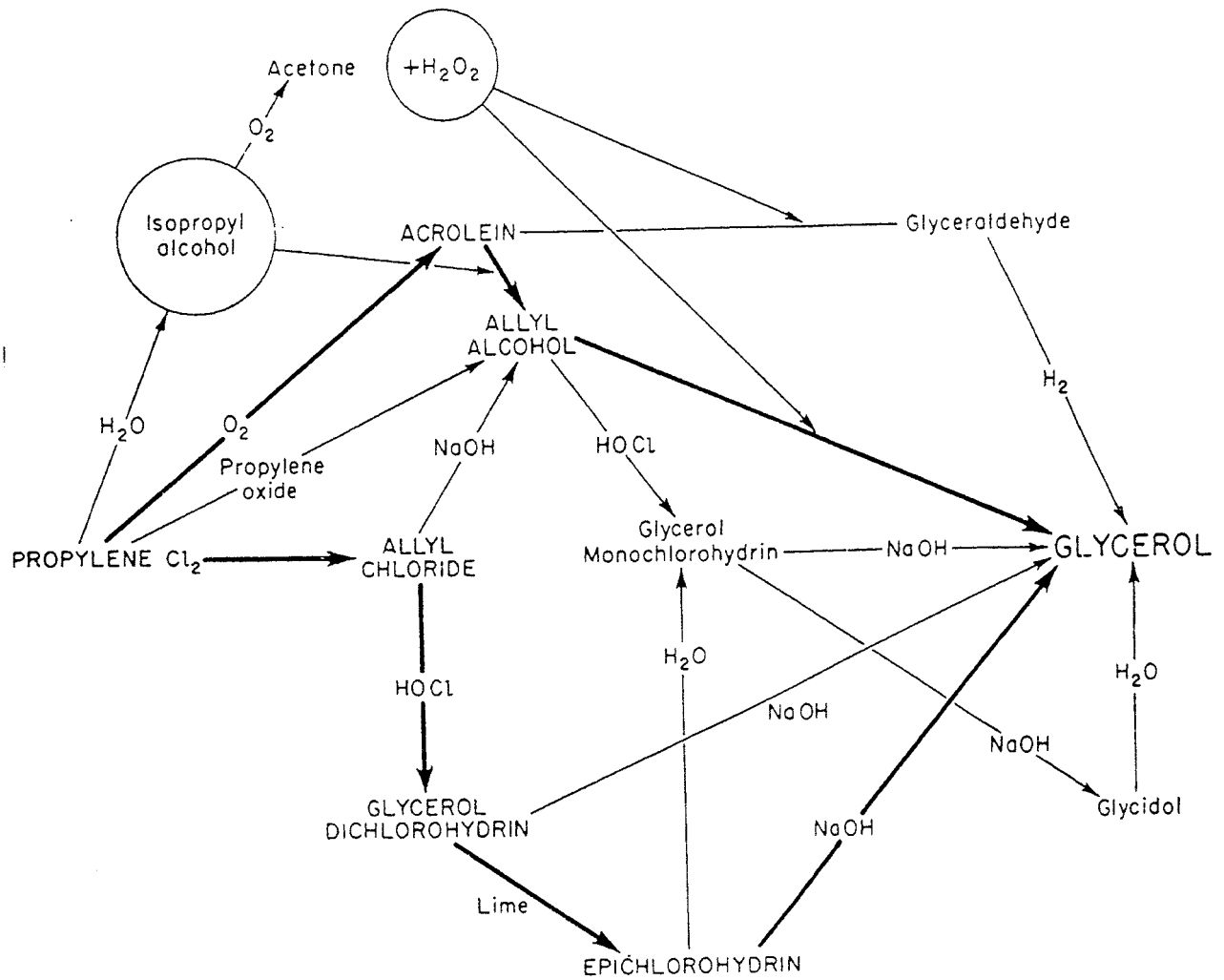

Fig. 3.11. Routes for the synthesis of glycerin.

easily hydrated to monochlorohydrin and then hydrated to glycerin with caustic soda. The reactions are:

$$CH_3 \cdot CH{:}CH_2 + Cl_2 \rightarrow CH_2Cl \cdot CH{:}CH_2 + HCl \text{ (85 percent yield)}$$
$$CH_2Cl \cdot CH{:}CH_2 + HOCl \rightarrow CH_2Cl \cdot CHCl \cdot CH_2OH \text{ (95 percent yield)}$$
$$CH_2Cl \cdot CHCl \cdot CH_2OH + 2NaOH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH + 2NaCl$$

The overall yield of glycerin from allyl chloride is above 90 percent.

Another process for obtaining glycerin from propylene involves the following reactions, where isopropyl alcohol and propylene furnish acetone and glycerin (through acrolein) in good yields.

$$CH_3 \cdot CHOH \cdot CH_3 + \text{air} \rightarrow CH_3 \cdot CO \cdot CH_3 + H_2O_2$$
$$CH_3 \cdot CH{:}CH_2 + \text{air} \rightarrow CHO \cdot CH{:}CH_2 + H_2O$$
$$CHO \cdot CH{:}CH_2 + H_2O_2 \rightarrow CHO \cdot CHOH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH$$

Figure 29.11 illustrates the various methods of synthetic glycerin production.

In 1982 only Dow Chemical Co. was producing synthetic glycerin the the United States because of rising energy costs and the increase in supplies from soapmakers and imports of low-priced glycerin from Europe.

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Chapter 4

Fermentation Industries

HISTORICAL. Although the fermentation of fruits to alcohol was known to primitive humans, and although the making of various beverages out of fruits and grains has been well established for centuries, only during the past century has wider application of this procedure been recognized. Now scientists are directing the life processes of yeasts, bacteria, and molds to produce chemicals. The modern definition of industrial fermentation is any microbial process controlled by humans that produces useful products.

The foundation of the scientific understanding of fermentation, indeed of the action of all microorganisms, hence of their economic control, rests firmly upon the genius of one man, Louis Pasteur.[1] He showed that fermentation is directly caused by the life processes of minute organisms. By understanding how these microorganisms function and by recognizing that varieties of yeasts, for example, act differently and that the environment fundamentally affects even a given strain, these processes of fermentation can be controlled in an exact scientific manner.

Microorganisms, which include bacteria, yeasts, and molds, feed upon organic materials. It is this feeding that interests the manufacturer, for if they are supplied with the necessary energy foods, together with other needed nutrients, these microvegetative organisms will not only grow and multiply but will change the food into other chemical substances.

Yeasts and bacteria are unicellular and of very small dimensions. Yeasts are irregularly oval and around 0.004 to 0.010 mm in diameter. Bacteria are smaller, mostly less than 0.007 mm in the longer dimension, and more diverse in shape. Many of them, bacilli, are rod-shaped. Yeasts multiply by budding, and bacteria by binary fission. Molds are multicellular filaments and increase by vegetative growth of the filament. Sporulation provides for the next cycle, as it does also with many bacteria. The vegetative reproduction cycle of these bacteria and of yeast is short—measured in minutes. Because of this, they multiply exceedingly fast.

The production of lactic acid in 1880 was the beginning of industrial fermentation to produce a useful product other than alcohol. During World War I, Chaim Weizmann developed a fermentation process to convert corn to acetone and *n*-butanol. Acetone was necessary for the manufacture of cordite for use in ammunition and without this fermentation process Britain would have had a serious shortage of ammunition. Citric acid and gluconic acid were successfully produced between 1920 and 1940, but the young petrochemical industry then made most fermentation processes uneconomical. During World War II, the discovery of antibiotics, such as penicillin, set the stage for the great technological advances in controlling microbiological processes that are commonly used today.

[1]Current Developments in Fermentation, *Chem. Eng.* 81 (26) 98 (1974); ECT, 3d ed., vol. 9, 1980, pp. 861–880.

USES AND ECONOMICS. Many fermentation processes are in direct competition with strictly chemical syntheses. Alcohol, acetone, butyl alcohol, and acetic acid produced by fermentation have largely been superseded by their synthetic counterparts. Almost all the major antibiotics are obtained from fermentation processes. Dextran is another fermentation product. The microbiological production of vitamins has also become economically important. In Chap. 6 antibiotics, hormones, and vitamins are presented together with several flowcharts. Table 4.1 lists some of the products produced by fermentations. The enzyme glucose isomerase is used to produce high fructose syrup from corn, and proteases produced from mold enzymes are used to coagulate protein in milk to produce cheese.

Fermentation under controlled conditions involves chemical conversions.[2] Some of the more important processes are: *oxidation*, e.g., alcohol to acetic acid, sucrose to citric acid,

[2]Wailen, Stodola, and Jackson, *Type Reactions in Fermentation Chemistry*, Dept. of Agriculture, Agricultural Research, 1959 (hundreds of reactions under 14 types).

***Table* 4.1** Survey of Some Important Fermentations

Food and Beverages	Industrial	Pharmaceuticals (antibiotics)
Beer (Y)	Acetic acid	Amphotericin
Bread (Y)	Acetone	Bacitracin
Cheese (M or B)	Amino acids	Bleomycin
Cocoa (B and Y)	Aspartic acid	Candicidin
Coffee (M)	2,3-Butanediol	Capreamycin
MSG (B)	*n*-Butyl alcohol	Cephalosporin C
Olives (B)	Carbon dioxide	Chloramphenicol
Pickles (B and Y)	Citric acid	Chlortetracycline
Sauerkraut (B)	Dextran	Colistin
Single-cell protein (Y, B, or M)	Dihydroxyacetone	Cycloheximide
Tea	Ethyl alcohol	Cycloserine
Vinegar (B and Y)	Fumaric acid	Dactinomycin
Wine (Y)	Fusel oil	Doxorubicin
Whiskey	Gallic acid	Erythromycin
Vitamins	Gluconic acid	Gentamycin
Ergosterol (Y, M)	Glycerol	Griseofulvin
Gibberellins (B)	Isoleucine	Kanamycin
Riboflavin (B, Y)	Itaconic acid	Lincomycin
Vitamin A (B)	2-Ketogluconic acid	Mithramycin
Vitamin B_2 (Y)	5-Ketogluconic acid	Mitomycin C
Vitamin B_{12} (B, M)	Lactic acid	Neomycin
Enzymes	Lysine	Novobiocin
Amylases	Succinic acid	Nystatin
Cellulase	Sulfuric acid (from sulfur)	Oleandromycin
Dextranase	Tartaric acid	Oxytetracycline
Glucose isomerases	Valine	Paromomycin
Lactase	Yeast	Penicillins
Invertase	Xanthan	Polymyxin
Maltase		Rigamycin
Pectinase		Spectinomycin
Proteases		Streptomycins
		Tetracycline
		Vancomycin

Y, Yeast; B, bacteria; M, molds.

and dextrose to gluconic acid; *reduction*, e.g., aldehydes to alcohols (acetaldehyde to ethyl alcohol), and sulfur to hydrogen sulfide; *hydrolysis*, e.g., starch to glucose, and sucrose to glucose and fructose and on to alcohol; and *esterification*, e.g., hexose phosphate from hexose and phosphoric acid. Actually, certain chemical conversions can be carried out more efficiently by fermentation than by chemical synthesis.

Many chemical reactions caused by microorganisms are very complex, however, and cannot easily be classified; so the concept of fermentation itself as a chemical conversion has been developed. According to Silcox and Lee,[3] the five basic prerequisites of a good fermentation process are:

1. A microorganism that forms a desired end product. This organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yields.
2. Economical raw materials for the substrate, e.g., starch or one of several sugars.
3. Acceptable yields.
4. Rapid fermentation.
5. A product that is readily recovered and purified.

According to Lee, certain factors should be stressed in relation to the fermentation chemical-conversion or unit-process concept, such as microorganism, equipment, and the fermentation itself. Certain critical factors of the fermentation are pH, temperature, aeration-agitation, pure-culture fermentation, and uniformity of yields.[4] The microorganisms should be those which flourish under comparatively simple and workable modifications of environmental conditions.

In understanding, hence in correctly handling, microorganisms, a sharp differentiation should usually be made between the initial growth of a selected strain of these organisms to a sufficient quantity and the subsequent processes whereby, either through their continued living or as a result of enzymes previously secreted, the desired chemical is manufactured. To obtain a maximum chemical yield, it is frequently advisable to suppress additional increase in the quantity of the microorganism. Highly specialized microbiologists are engaged in selecting and growing the particular strain of an organism that has been shown to produce the chemical wanted with the greatest yields, the least by-product, and at the lowest cost.

No longer will just any yeast do to make industrial alcohol or a fermented beverage; not only are wild yeasts exlcuded, but a special strain must be used.

The yeasts, bacteria, and molds employed in fermentation require specific environments and foods to ensure their activities. The concentration of the sugar or other food affects the product. The most favorable temperature varies (5 to 40°C), and the pH also has great influence. Indeed, the bacteriologist has developed acid-loving yeasts, so that wild yeasts, not liking acidic conditions, do not flourish. Some microorganisms require air (aerobic), and others go through their life processes without air (anaerobic). Certain anaerobes neither grow nor function in the presence of air. In directing these minute vegetative organisms, conditions can be controlled to encourage the multiplication of the organism first, and then its *functioning*, either directly or through the *enzymes* secreted. How important this is can be seen from the knowledge that to grow 1 g of yeast (dry basis) requires 1.5 to 2.0 g of monosaccharide per day, and 6 g to maintain it. By virtue of this growth, organic catalysts, or *enzymes*, are frequently formed that directly cause the desired chemical change. During the growth period, in addition to the primary, or energy food, such as monosaccharides for yeast,

[3]Silcox and Lee, Fermentation, *Ind. Eng. Chem.* 40 1602 (1948).

[4]Humphrey, Fermentation Technology, *Chem. Eng. Prog.* 73 (5) 85 (1977).

various *nutrients* are needed, such as small amounts of phosphates and nitrogenous compounds, as well as favorable pH and temperature. Finally, certain substances poison these microorganisms and their enzymes. Even the alcohol formed by the yeasts eventually reaches a concentration (varying with the yeast from about 2 to 15%) that will suppress the activity of the organism and its enzymes.

More than 23,000 t/year of antibiotics are produced worldwide.[4a] Other fermentation products produced in large quantities (more than 23,000 t/year) are enzymes, organic acids, solvents, vitamins, and amino acids. The largest volume materials are monosodium glutamate and citric acid.[5]

INDUSTRIAL ALCOHOL

Industrial alcohol was an outgrowth of alcoholic beverages, but now it has become important by virtue of its economically useful properties as a solvent and for synthesis of other chemicals. Alcohol is sold as tax-paid[6] alcohol or, much more widely, as nontaxed denatured alcohol. The completely denatured formulas are admixtures of substances which are difficult to separate from the alcohol and which smell and taste bad, all this being designed to render the alcohol nonpotable. Such completely denatured alcohol is sold widely without bond. Factories find it an essential raw material. A typical completely denatured alcohol formula follows:

To every 100 gal of ethyl alcohol of not less than 160 proof add:
0.125 gal of Pyronate or a compound similar thereto.
0.50 gal of acetaldol (β-hydroxybutyraldehyde), 2.50 gal of methyl isobutyl ketone, and 1.00 gal of kerosene.

The federal government has recognized the needs of industry for alcohol in such form that it can enter into specialized manufacturing processes where the denaturants used in completely denatured alcohol would interfere. Since 1906, when the first U.S. denatured alcohol law was passed, many formulas for specially denatured alcohol have been approved by the federal authorities. Such special formulas are limited to certain designated processes and are manufactured, stored, and used under bond to prevent unlawful consumption. However, the 40 approved special formulas under their authorized uses enter into an exceedingly broad section of the entire industrial life of the nation.[7] These special denatured alcohols are also

[4a]t = 1000 kg.

[5]ECT, 3d ed., vol. 9, 1980, p. 877.

[6]The federal tax is $10.50 per proof gallon, hence $19.95 on a gallon of 190-proof alcohol. The total sum collected by the federal alcohol tax unit was $5,612,714,948 in 1978, largely from beverages. A *proof gallon* (tax gallon or 3.785 L) signifies a gallon containing 50% alcohol by volume; 100 volumes of 100-proof alcohol contain 50 volumes of absolute alcohol and 53.73 volumes of water owing to volume contraction. Ordinary alcohol of 95% strength is thus 190-proof alcohol, and pure anhydrous alcohol is 200 proof. The lower limit of alcohol dilutions which burn by direct ignition at ordinary temperatures is about 100-proof. A *wine gallon* is a measure of volume (3.785 L) of any proof.

[7]Withdrawals of specially denatured alcohol in 1978 amounted to 222.3×10^6 wine gallons and only 1.14×10^6 wine gallons of completely denatured alcohol.

nonpotable, but the denaturants are easier to remove than those in completely denatured alcohol. Typical specially denatured formulas are:[8]

To every 100 gal of 190-proof ethyl alcohol add:

SD No. 1. Approved wood alcohol, 5 gal. Withdrawals for authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.

SD No. 2B. Benzene, 0.5 gal. Withdrawals for authorized uses: plastics, dehydrations, explosives, food products, chemicals, etc.

SD No. 29. 100% acetaldehyde, 1 gal, or an alcoholic solution of acetaldehyde (20%), 5 gal. Withdrawals for authorized uses: manufacturing acetaldehyde, acetic acid, esters, ethers, etc.

In industrial nomenclature alcohol means ethyl alcohol, or ethanol (C_2H_5OH). It is sold by the gallon, which weighs 4.082 kg and contains 95% C_2H_5OH and 5% H_2O, both by volume at 15.56°C.[9] No distinction is made concerning the source of the alcohol, i.e., whether from fermentation or from synthesis.

USES AND ECONOMICS. Alcohol is second only to water in solvent value and is employed in nearly all industries. In addition, it is the raw material for making hundreds of chemicals, such as acetaldehyde, ethyl acetate, acetic acid, ethylene dibromide, glycols, ethyl chloride, and all ethyl esters.

The use of fermentation alcohol in motor fuel has been the subject of much controversy.[10] Proponents argue that alcohol, made from renewable, biological materials, can be used to help make the United States less dependent upon foreign sources of petroleum. They also claim it can be used as a method of utilizing much surplus grain and waste biomass materials. In 1980 the U.S. government announced an ambitious program to quadruple the use of alcohol for fuels production to 1.9×10^9 L/year by the end of 1981 and to 42×10^9 L/year by 1990. The goal is to displace 10 percent of the nation's gasoline with gasoline-alcohol fuels (gasohol).

Opponents claim that to produce that much alcohol would require not only using all the surplus grain available but also radically new technology to convert economically wood, cellulose, and other starchy wastes to alcohol. One of the chief difficulties in using alcohol in gasoline is that the usual 95% ethanol is not miscible with gasoline. Only absolute or 99.5% alcohol will mix with gasoline for gasohol; this requires costly extra processing, because simple distillation will not produce ethanol above 95% concentration. Many new methods for lower cost distillation or other ways of removing the water in the alcohol have been proposed, but so far absolute alcohol continues to cost more to produce than gasoline.[11]

At the present time, 1982, ethanol is being used as an octane booster for gasoline, and a small amount is being consumed as gasohol. However, because of government subsidies, the

[8] *Formulas for Denatured Alcohol*, U.S. Revenue Service, Part 12 of Title 26, Federal Regulations, 1961.

[9] This corresponds to 92.423% of ethyl alcohol by weight. However, when alcohol percentage strength is given, it usually refers to percentage by volume.

[10] Is the U.S. Ethanol Goal Feasible? *Chem. Eng.* 87 (21) 53 (1980); Mendelsohn and Wettstein, Ethanol from Wood, *Chem. Eng.* 88 (12) 62 (1981).

[11] *Chemtech* 11 (12) IBC (1981); *Chem. Eng.* 88 (11) 29 (1981); *Chem. Eng. News* 59 (11) 15 (1981); *Chem. Eng.* 87 (23) 103 (1980); *Chem. Week* 13 (3) 10 (1983); Fong, Jones, and Semrau, Costs of Producing Ethanol from Biomass, *Chem. Eng. Prog.* 76 (9) 39 (1980); Standiford, Energy Conservation in Alcohol Production, *Chem. Eng. Prog.* 79 (1) 35 (1983).

cost of fermentation alcohol is now low enough for it to be competitive with petroleum-based synthetic ethanol. In 1983 the U.S. synthetic alcohol capacity was 8.1×10^8 kg and production was only 4.5×10^8 kg. The price of synthetic ethanol was 61 to 65 cents per kilogram, about the same as that of fermentation ethanol for solvent purposes.[12]

Manufacture

RAW MATERIALS. The manufacture of alcohol from ethylene and other synthetic manufacturing procedures, now the most important source, is discussed in Chap. 38 and illustrated by the flowchart in Fig. 38.9. Alcohol from cellulosic materials, wood, wood wastes, and sulfite liquors, is considered in Chap. 32, principally under wood hydrolysis. This procedure is not competitive except under special conditions, largely because of the cost of converting cellulosic materials to fermentable sugars. Of the 760×10^6 L of industrial ethanol (excluding fuels) produced in the United States in 1981 less than 2 percent was made by fermentation. Continually changing prices of the various carbohydrate feedstocks available can cause major changes in the ratio and it is certainly possible that petroleum shortages will make this process important again as it once was when cheap Cuban molasses was used as the fermentable material. Corn is considered to be the most promising raw material for fermentation to alcohol, especially for gasohol. The yield of 25 kg of corn will be 9 to 11 L of alcohol. Table 4.2 shows the production of ethyl alcohol from various raw materials.

The principal reactions in alcohol fermentation are:

EQUATIONS OF MONOSACCHARIDE PRODUCTION[13]

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

[12]Key Chemicals, *Chem. Eng. News* 59 (45) 14 (1981).

[13]If sugar (sucrose) is fermented it must first be inverted by the enzyme invertase to yield glucose and fructose which can then be converted to alcohol.

Table 4.2 1978 Ethyl Alcohol Production by Type of Raw Materials (thousands of liters of 95% alcohol)

Raw Material	Liters
Ethyl sulfate	1,445,851
Ethylene gas	518,627
Grain and grain products	6,045
Redistillation	11,253
Molasses	78,857
Sulfite liquors	27,842
Whey	125
Total	2,088,600

SOURCE: *Alcohol and Tobacco Summary Statistics*, ATF Publication P1323.1 (4-81), 1978.

EQUATIONS OF FERMENTATION[14]

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{Alcohol}}{C_2H_2O_5OH} + 2CO_2 \qquad \Delta H = -130 \text{ kJ}$$

$$\underset{\text{Monosaccharide}}{2C_6H_{12}O_6} + H_2O \rightarrow \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH} + 2CO_2 + \underset{\text{Glycerin}}{2C_3H_8O_3}$$

A small amount of glycerin is always found in alcohol fermentations. Toward the end of a fermentation, the acidity and the glycerin increase.

These are the classic Gay-Lussac equations for alcohol formation. They are the principal equations in an acid or low pH medium. When growing yeast for sale as such or for inoculation, the yield of alcohol is lower, since it is partly changed to CO_2 and H_2O. This fermentation, like so many industrial reactions, is much more involved than these simple reactions indicate. Probably the first step is phosphate hexose ester formation, followed by a split in the six-carbon chain. The fusel oil (mixed amyl alcohols with some propyl, butyl, and hexyl alcohols and esters), amounting to 3 to 11 parts per 1000 parts of alcohol, obtained from yeast fermentations, is thought to be furnished by the protein materials in the mash fermented.

ENERGY REQUIREMENTS, UNIT OPERATIONS, CHEMICAL CONVERSIONS. Plant procedures require steam heating for distillation, power for pumping, and water for condensation, and occasionally for cooling during the exothermic fermentation. Several new methods of handling the various steps with the aim of improving energy efficiency have been proposed.[15] Conventional corn units to produce anhydrous alcohol demand 13 kg of steam per liter of product. Some of the newer processes claim to cut this to 2 kg per liter.

The manufacture of alcohol, as presented in Fig. 4.1, can be broken down into the following steps. The main steps in the competitive manufacture of alcohol from petroleum cracking (cf. Fig. 38.9), are shown in parallel comparisons.

Fermentation Alcohol	Alcohol from Ethylene
Transportation of corn or molasses	Liquefaction of petroleum gases containing ethylene
Storage of corn or molasses	Rectification to produce pure ethylene and pure ethane
Grinding, etc., of corn	Dehydrogenation of ethane to ethylene
Hydrolysis by heating of cornmeal with malt or acid to make mash	Hydration over a catalyst
Growth of inoculating cultures	Distillation of alcohol from partially converted ethylene
Fermentation of diluted inverted molasses or of corn mash	Rectification and purification of alcohol
Distillation of alcohol from "beer"	
Rectification and purification of alcohol	
Recovery of by-products, e.g., CO_2, feed, potash salts	

[14]Prescott and Dunn, *Industrial Microbiology*, 3d ed., chap. 4, McGraw-Hill, New York, 1959; Michaelis, Chemistry of Alcoholic Fermentation, *Ind. Eng. Chem.* 27 1037 (1935).

[15]Low Energy Processes Vie for Ethanol-Plant Market, *Chem. Eng.* 87 (6) 57 (1980).

MAKING OF INDUSTRIAL ALCOHOL.[16] The flowchart in Fig. 4 .1 shows the various operations involved in changing corn to alcohol. The corn is degerminated, dehulled, and milled, either wet or dry. The milled corn is conveyed to the cooker. Cooking is necessary to gelatinize the ground grain so that the barley malt amylases can convert the starch to fermentable sugars. The cookers may be batch or continuous and are operated under pressure. In the continuous process the grain is precooked for 1 to 5 min with water and stillage (the dealcoholized, fermented beer that is discharged from the bottom of the beer still). The mash is continuously fed to a steam heater that instantaneously raises the temperature to 175°C. The mash is passed through a series of pipes and discharged through a relief valve into a flash chamber. Time in the cooker is about 1.5 min and the pressure is maintained at 60 to 100 kPa gage. The temperature of the mash drops to about 60°C in the flash chamber.

The gelatinized (cooked) grain mash is mixed with malted barley and water. The mix is pumped through a pipeline (converter) for 2 min at 60°C and then is sent to the fermentors through pipe coolers. The starch is hydrolyzed to about 70% maltose and 30% dextrins in the short time in the converter. Stillage (20 to 25% of the final mash volume) from the beer still is added to the converted grain mash prior to fermentation to lower the pH, furnish nutrients for the yeast, and to add buffering action.

Meanwhile a charge of the selected yeast (about 5 percent of the total volume) has been growing in the yeast tub on a corn-barley malt mash which has been previously sterilized under pressure and cooled. Bacteriologists have cultivated a strain of yeast that thrives under acid conditions whereas wild yeasts and bacteria do not.

The mash is pumped into the fermentor and the yeast added as soon as 10 percent of the malt has been pumped. The initial pH is adjusted to 4.8 to 5.0 with sulfuric acid and/or stillage. As the reaction indicates, fermentation is exothermic, so cooling may be necessary to ensure that the maximum temperature does not exceed 32°C. The time of the fermentation cycle may vary from 40 to 72 h.

The liquors in the fermentors, after the action is finished, are called *beer*.[17] The alcohol is separated by distillation. The beer, containing from 6.5 to 11% alcohol by volume, is pumped

[16]Underkofler, *Industrial Fermentations*, vol. I, Chem. Publ. Co., New York, 1954.

[17]This is a general term applied to the result of any such fermentation, whether it results finally in industrial alcohol or the beverage beer, or whiskey, or butyl alcohol and acetone; ECT, 3d ed., vol. 9, 1980, p. 355.

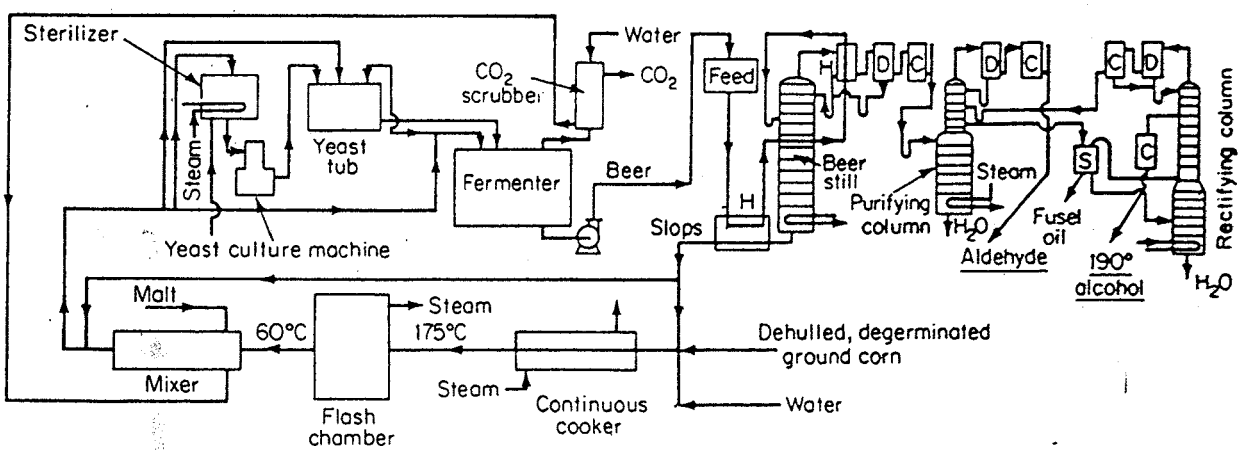


Fig. 4 .1. Flowsheet for industrial alcohol. KEY: C, condensor; D, dephlegmator; H, heat exchanger; S, separator.

to the upper sections of the beer still, after passing several heat exchangers. As the beer passes down the column, it gradually loses its lighter boiling constituents. The liquid discharged from the bottom of the still through a heat exchanger is known as *stillage*. It carries proteins, residual sugars, and in some instances, vitamin products so it is frequently evaporated and used as a constituent of animal feed. The overhead containing alcohol, water, and aldehydes passes through a heat exchanger to the partial condenser, or dephlegmator, which condenses sufficient of the vapors to afford a reflux and also to strengthen the vapors that pass through to the condenser, where about 50% alcohol, containing volatiles, or aldehydes, is condensed. This condensate, frequently known as the high wines, is conducted into the aldehyde, or heads, column, from which the low-boiling impurities are separated as an overhead. The effluent liquor from part way down the aldehyde column flows into the rectifying column.

In this third column the alcohol is brought to strength and finally purified in the following manner: The overhead passing through a dephlegmator is partly condensed to keep the stronger alcohol in this column and to provide reflux for the upper plates. The more volatile products, which may still contain a trace of aldehydes and of course alcohol, are totally condensed and carried back to the upper part of the aldehyde still. Near the top of the column 95 to 95.6% alcohol is taken off through a condenser for storage and sale. Farther down the column, the higher boiling fusel oils are run off through a cooler and separator to a special still, where they are rectified from any alcohol they may carry before being sold as an impure amyl alcohol for solvent purposes. The bottom of this rectifying column discharges water.

Alcohol-water mixtures are rectified to increase the strength of the alcohol component by virtue of the composition of the vapors being stronger in the more volatile constituent than the liquid from which these vapors arise. This is shown quantitatively by the curves in Fig. 4.2, where the composition of the vapor in equilibrium with the liquid is on a horizontal line. However, alcohol cannot be made stronger than 95.6% by rectification, because, as can be seen from Fig. 4.2, water forms a binary constant-boiling mixture of this composition which boils slightly lower than absolute, or anhydrous, alcohol. The principles shown here are the basis of the strengthening of the more volatile constituent of any liquid mixture by distillation.

ABSOLUTE ALCOHOL[18]

Anhydrous alcohol was formerly made by absorbing the 4 to 5% water present in 95 to 96% industrial alcohol using quicklime, with subsequent distillation. This process was expensive, and although it produced a very high quality of anhydrous alcohol, it has now been superseded. Ethyl alcohol and water form an azeotrope which is 95% by volume alcohol. Various methods are in use and/or have been suggested for removing the last 5% of water to produce 100% alcohol. Table 4.3 lists a number of separation routes and also shows the energy necessary to accomplish the water removal.

The oldest method is distillation of the 95% azeotrope using a third component which forms a minimum constant-boiling mixture boiling at a lower temperature than the 95% alcohol or

[18]This is practically 100% ethyl alcohol, frequently known as *absolute* alcohol, but since the absence of water is more notable than that of other impurities, the term *anhydrous* is preferred by some.

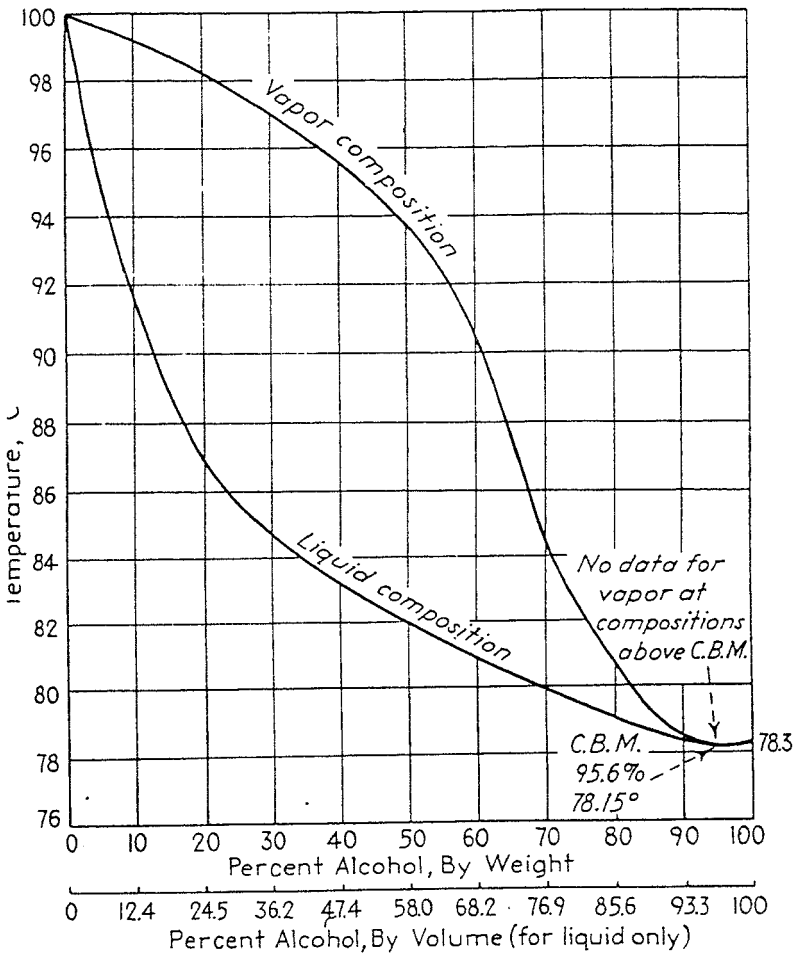


Fig. 4.2. Temperature versus composition of vapor and liquid for alcohol-water at 101 kPa.

the water. Figure 4.3 shows the three binary minimum constant-boiling mixtures in the system, using benzene as the third component (entrainer), as well as two homogeneous mixtures, a heterogeneous (water and benzene) one, and a ternary one. The ternary mixture is the lowest-boiling composition in the system, boiling at 64.85°C as shown at point F. The starting composition of the mixture must lie on the straight line CF to ensure that removal of the constant-boiling mixture will leave anhydrous alcohol in the still. If the starting mixture is made up by adding benzene to 95% alcohol, the starting composition must also lie along the line EB. Therefore, the intersection G represents the starting composition. If enough benzene is added to 95% alcohol to bring the total composition to point G, continuous distillation gives the ternary constant-boiling mixture (bp 64.85°C) at the top of the column and absolute alcohol (bp 78.3°C) at the bottom of the column.

An important feature[19] of the process is separation of the condensate into two liquid layers, represented in Fig. 31.3 by points M and N. The ratio of the top layer N to the bottom layer M is equal to MF/FN, or 84:16. The compositions involved are shown in Fig. 4.4, which also illustrates how this process functions. These same principles of distillation in multicomponent systems, involving various constant-boiling mixtures, are used for dehydrating other

[19]Guinot and Clark, Azeotropic Distillation in Industry, *Trans. AIChE* (London) 16 189 (1938).

Table 4.3 Separation Routes to Absolute Alcohol

Type of Separation	Ethanol, % Initial	Ethanol, % Final	Process	Energy Needed, kJ/L
Complete	10	100	Conventional "dual" distillation	7600
Complete	10	100	Extraction with CO_2	2200–2800
Complete	10	100	Solvent extraction	1000[a]
Complete	10	100	Vacuum distillation	9800[b]
To azeotrope	10	95	Conventional distillation	5000
To azeotrope	10	95	Vapor recompression	1800[a]
To azeotrope	10	95	"Multieffect" vacuum	2000[c]
Azeotropic	95	100	Conventional azeotropic distillation	2600
Azeotropic	95	100	Dehydration via adsorption	335[d]
Azeotropic	95	100	Low-temperature blending with gasoline	800[e]
Azeotropic	95	100	Molecular sieve	1300–1750
Other	3	10	Reverse osmosis	140

[a]Figure given is the thermal energy required to provide mechanical energy for the process.

[b]For single-column distillation.

[c]For three-column distillation.

[d] For drying with CaO; energy requirements using fermentable grains would be considerably less.

[e]Results directly in production of gasohol.

SOURCE: Battelle Pacific Northwest Laboratories, *Chem. Eng.* 88 (11) 29 (1981).

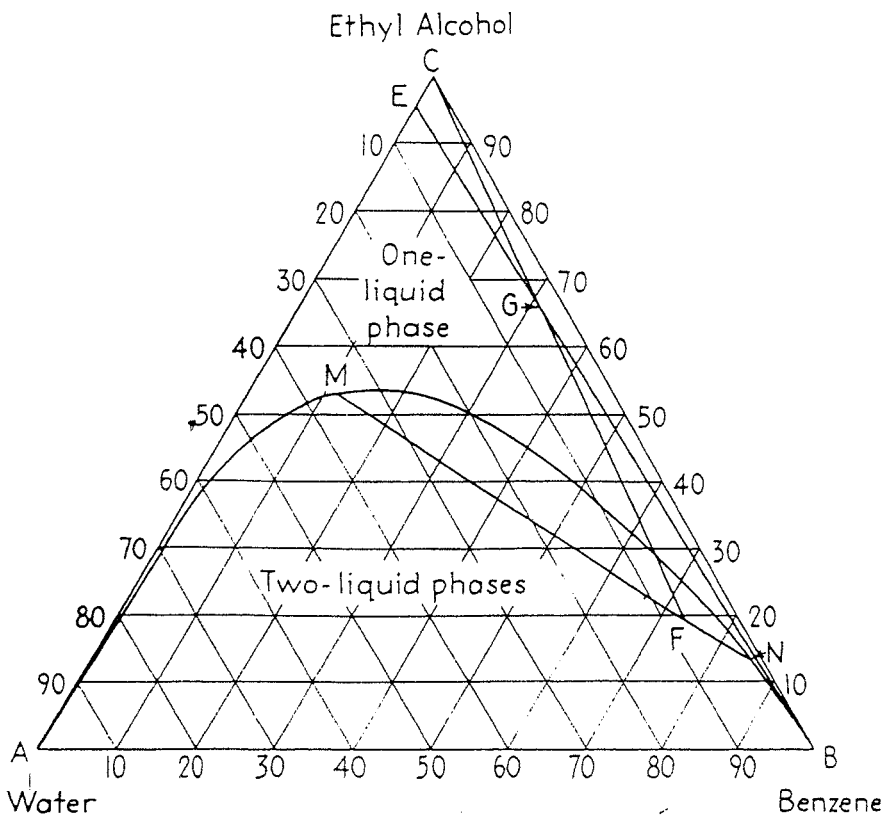
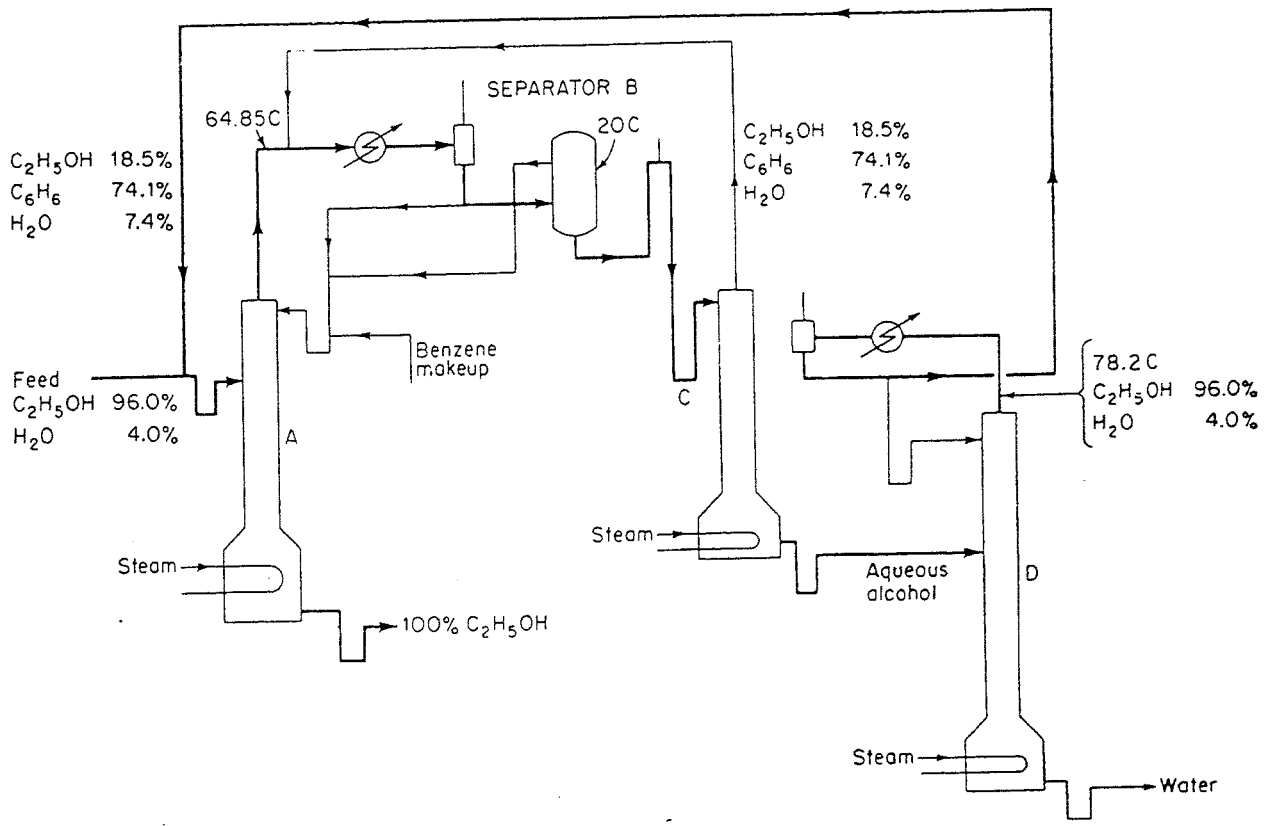


Fig. 4.3. Ternary diagram of the liquid system water-alcohol-benzene.



	TOP LAYER	BOTTOM LAYER
	SEPARATOR EQUILIBRIUM	
Vol. % overhead	84.0	16.0
	COMPOSITIONS, %	
C_2H_5OH	14.5	53.0
C_6H_6	84.5	11.0
H_2O	1.0	36.0

Fig. 4.4. Dehydration of 96% ethanol to absolute alcohol by azeotrope distillation with benzene at 101 kPa. Column A has 95% alcohol fed into it. The ternary azeotrope is taken overhead in this column, and absolute alcohol is obtained as a bottoms product. The overhead vapors are condensed and passed to separator (decanter) B, in which two liquid layers form. The upper layer, rich in benzene, is returned to column A as reflux, and the lower layer is fed to column C which produces the ternary azeotrope as the overhead product and benzene-free aqueous alcohol as the bottoms product. This latter product is fed to column D which produces by ordinary distillation an overhead product of 95% alcohol and a bottoms product of nearly pure water. The benzene is recycled continuously in this system, and it is necessary only to make up the benzene losses from the system. This withdrawing agent is used over and over again with a loss that should not exceed 0.5 percent of the volume of the anhydrous alcohol produced. [*Perry, p. 13-42; Chem. Eng.* **67** *(10) 129 (1960).*]

organic liquids, such as propyl alcohol and for removing the water formed in sulfonations (benzenesulfonic acid) and esterifications (ethyl acetate).[20] The fundamentals of distillation are presented because of the extensive data on alcohol that are available.

The data in Table 4.3 clearly show that this conventional "dual" distillation process requires much more energy than any of the other possible methods of removing the last water in the alcohol, with the exception of vacuum distillation. One of the newer proposals is to use cellulose or cornmeal to adsorb the water. Aluminum oxide and silicon oxide adsorbents have also been used. Another promising method is to use liquid CO_2 to extract the ethanol and then depressurizing to flash off CO_2. Other solvents, such as dibutyl phthalate, which are immiscible with water but are good solvents for ethanol, are under investigation.

Interest in cutting energy demand for production of 100% alcohol is very great because of the proposed use of gasohol.[21] The energy liberated by burning 1 L of 100% alcohol is about 23 MJ and thus, because many of the present processes for fermenting and distilling corn-derived alcohol consume up to 42 MJ/L, the energy consumed in preparing the alcohol is greater than its potential energy content. To make gasohol a viable economic product will require processes that can produce it with much smaller amounts of energy than have been used in the past. The average total energy consumption for the new processes is 11 to 12.5 MJ/L; several of the processes claim much lower energy demands.

BEERS, WINES, AND LIQUORS

The making of fermented beverages was discovered by primitive humans and has been practiced as an art for thousands of years. Within the past century and a half it has evolved into a highly developed science. A good brewer has to be an engineer, a chemist, and a bacteriologist. In common with other food industries, the factors taste, odor, and individual preference exist to force the manufacturer to exert the greatest skill and experience in producing palatable beverages of great variety. In the last analysis, the criterion of quality, with all the refinements of modern science, still lies in the human sensory organs of taste, smell, and sight.

Alcoholic beverages are divided into three groups: malt liquors, fermented wines, and distilled liquors. Beer and ale require malted (germinated) grain to make the carbohydrates fermentable, wines are produced by the action of yeast on the sugar of fruit, and distilled liquors are fermented liquors which are then distilled to increase the alcoholic content.

USES AND ECONOMICS. As Table 4.4 indicates, many millions of gallons of alcoholic beverages are manufactured in the United States each year. The amount of wine production has been increasing rapidly in recent years. In 1981[22] the consumption of malt beverages was 95.8 L, wine and brandy, 8.7 L, and distilled spirits, 11 L, all per capita (adult).

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[20]Hoffman, *Azeotropic and Extractive Distillation*, Interscience, New York, 1964.

[21]Black, Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol, *Chem. Eng. Prog.* 76 (9) 78 (1980); Low Energy Processes Vie for Ethanol-Plant Market, *Chem. Eng.* 87 (6) 57 (1980); *Chem. Eng.* 88 (19) (1981); Lowering the Cost of Alcohol, *Science*, 206 October 5, 1979, p. 641.

[22]*U.S. Industrial Outlook, 1982*, U.S. Department of Commerce.